

Trace analysis of lignin-phenols in speleothems by UHPLC-ESI-HRMS: Comparison of two lignin degradation methods

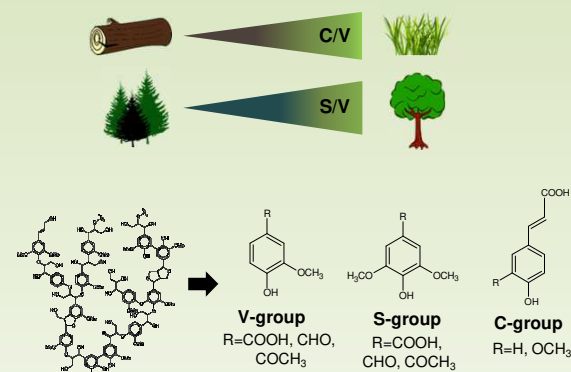
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1. Motivation

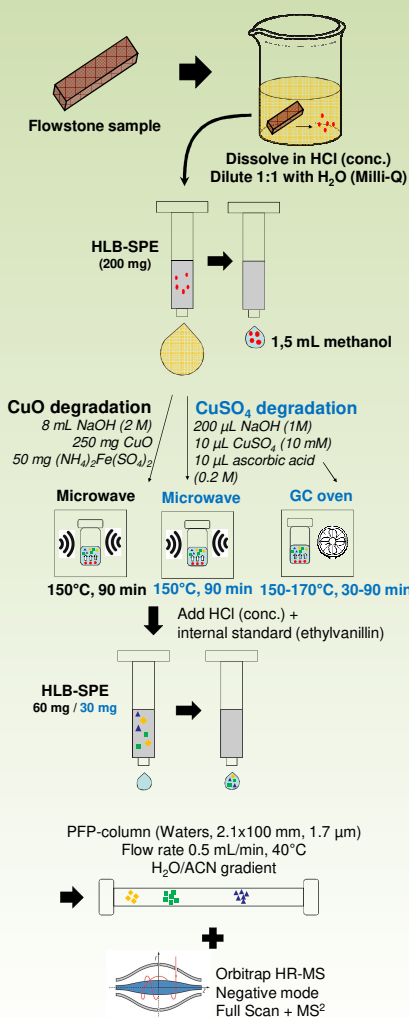
- Speleothems are valuable paleoclimate archives offering the possibility of precise dating up to 600,000 years back^{1,2}
- Biopolymer lignin as the main constituent of wood in higher plants consists of **three monomeric units**: sinapyl-, coniferyl-, and coumaryl alcohol
- Lignin is degraded by alkaline oxidation to its oxidized monomeric units - > **lignin oxidation products (LOP)**
- LOP classified into **vanillyl (V)-, syringic (S)-, and cinammyl (C) group**
- LOP composition (S/V and C/V ratio) provides information about **type of vegetation**³ e.g. above a cave



2. Aim of the project

- Adaptation of an alkaline oxidation method to the complex speleothem matrix
- Replacement of copper(II)-oxide by water-soluble copper-sulfate^{4,5}
- Improved **reproducibility** and lower detection and quantification limits
- Lower contaminations** and facilitated handling during sample preparation
- Decreased amount of chemicals and solvents -> **Green Chemistry**⁶
- Method comparison and application of the proper method to flowstone samples from a cave in the Southern Dolomites

3. Method



4. Method comparison

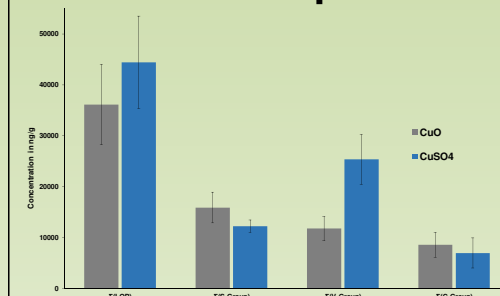


Fig. 1: Comparison of LOP-concentration after CuO- and CuSO₄ degradation. **No significant differences** among concentration and standard deviation (n=5) observable, therefore the **CuSO₄ method was applied** for further analysis. Further evaluation of a GC oven as an alternative to microwave-assisted degradation did not show significant concentration differences.

Results method comparison
 > CuSO₄ as catalyst
 > GC oven instead of microwave
 > 150°C for 90 minutes

Analysis of eight timely consecutive samples of a flowstone from a cave in the Southern Dolomites

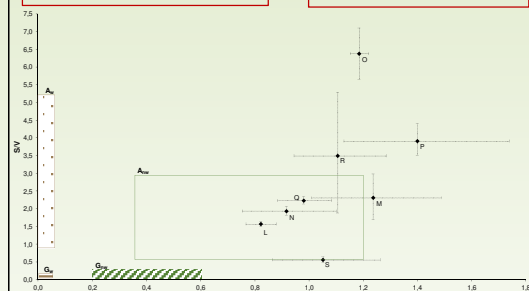


Fig. 3: Plotting of S/V to C/V ratios enables **classification** in woody (w) and non-woody (nw) angiosperms (A) and gymnosperms (G). Interpretation has to be conducted relatively to ΣLOPs. Samples showed rather characteristic composition of **non-woody angiosperms** → leaves and grasses of deciduous or flowering plants.

5. Application

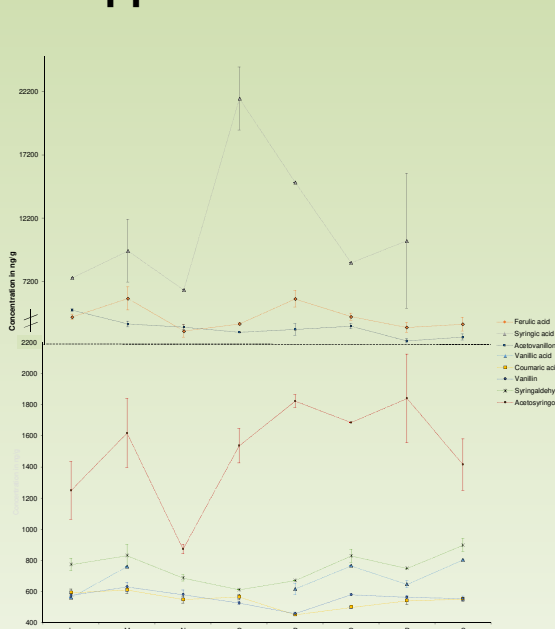


Fig. 2: Concentration profiles of LOPs along eight timely consecutive samples (L-S). Significantly high concentrations observable for syringic acid, ferulic acid and aceto-van in all samples. Highest standard deviations (n=3) observable for syringic acid (12-50%) and aceto-syr (3-16%).

LOP pair	Correl.	R
Van-acid / syr-ald	Pos	0.80
Van / coum-acid	Pos	0.75
Van / syr-acid	Neg	-0.62
Syr-ald / syr-acid	Neg	-0.70
Van-acid / aceto-syr	No	0.04
Aceto-van / syr-ald	No	0.03

6. Conclusion and outlook

- Adaptation of a **lignin degradation method to speleothem matrix** using CuSO₄ instead of Cu(II)-O → solvent volume decreased from 8 mL to 220 µL with **no significant concentration differences**
- Challenging method evaluation due to **lack of lignin standards** → high standard deviations among individual LOP concentrations and C/V ratios
- Application of method to eight timely consecutive flowstone samples: **correlations between single LOPs** observable → plotting of S/V to C/V showed **characteristic lignin compositions for non-woody angiosperms in all samples**
- Outlook:** a) further work to **evaluate high standard deviations** and optimize sample preparation with the new method
 b) other SPE material, **HILIC-MS**, analysis of **levoglucosan** as biomass burning marker in speleothems
 → current projects in working group

References:

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